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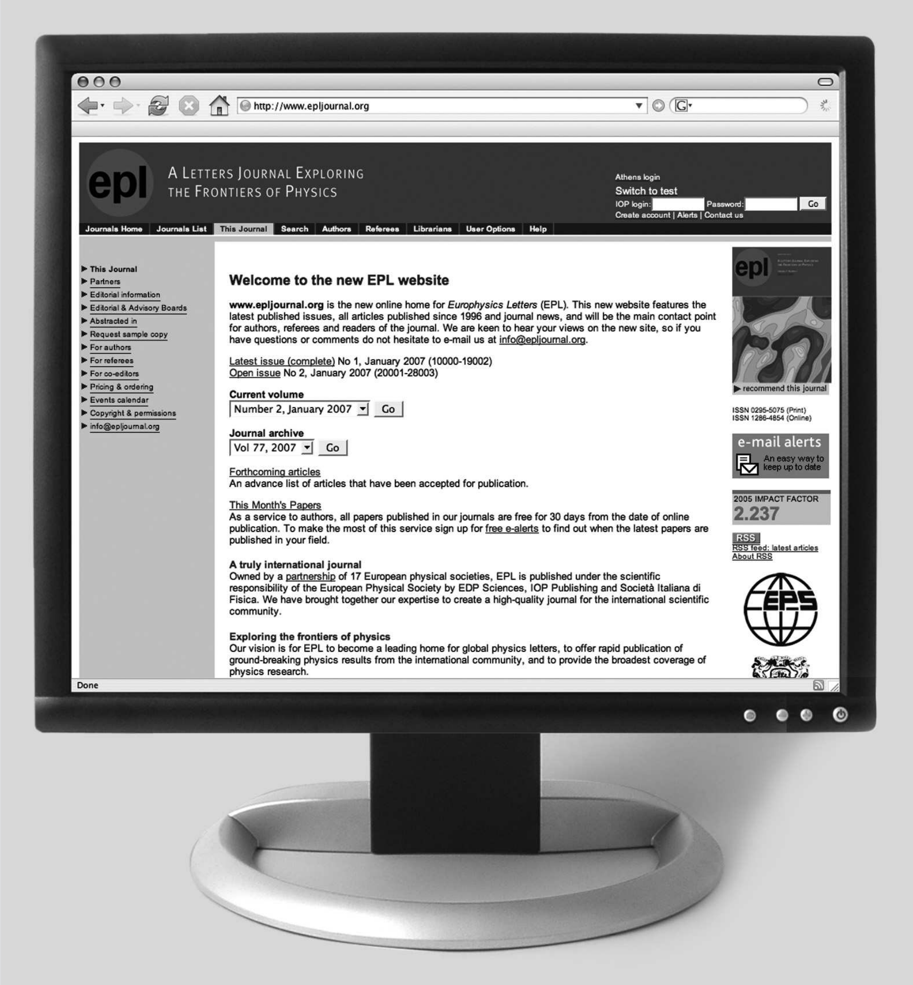

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Evidence for a temperature-driven structural transformation in liquid bismuth

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Abstract – The thermodynamic properties of liquid bismuth have been explored from the melting point to 1100 °C by high-resolution measurements of the density, the heat capacity and the static structure factor. These physical properties display a number of anomalies. In particular, we have observed evidence for the presence of a temperature-driven liquid-liquid structural transformation that takes place at ambient pressure. The latter is characterized by a density discontinuity that occurs at 740 °C. Differential thermal analysis measurements revealed the endothermal nature of this transformation. A rearrangement of liquid bismuth structure was found by neutron diffraction measurements, supporting the existence of a liquid-liquid transformation far above the liquidus.

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Introduction. – According to the conventional view, the structure of a liquid varies smoothly from the melting to the critical point [1]. This view has been challenged over the past two decades by the observation of anomalies of various physical properties as a function of pressure and temperature [2–5]. More recently, both experimental findings and theoretical predictions have suggested the presence of liquid-liquid phase transitions characterized by significant structural changes [6–16].

Possible liquid-liquid transitions under pressure have been reported for nonmetallic elements (*e.g.*, phosphorus, carbon) as well as for metals [3,6,16]. The existence of a temperature-driven phase transition at ambient pressure has been suggested only for liquid alloys [5,10,12,13]. The existence of a first-order phase transition has also been put forward in connection with the super-cooled metastable regime of water [14,15].

Group-V elements are potentially the most interesting in this context. A liquid-liquid phase transition (LLPT) having been observed in fluid phosphorus and a variety of abnormal physical properties in other elements of the group [17,18].

Bismuth displays a large number of allotropic forms as a function of temperature and pressure [19]. Its melting curve behaves anomalously with increased pressure. Across a wide range of physical properties, *e.g.*, sound velocity and electrical conductivity, liquid bismuth displays complex behavior [2,20–28]. Based on volumetric measurements, a phase diagram of liquid bismuth at pressures of 1–10 GPa was proposed in [2]. The structure of liquid bismuth, near its melting point, has also been studied by combined electronic-structure and molecular-dynamics calculations, which reproduced the main experimental findings [21]. However, detailed studies at temperatures well above the melting point have not been reported in the literature.

In the present work, we have carried out a detailed systematic mapping of the density, the thermal heat capacity and the structure factor of liquid Bi over a wide range of temperatures at atmospheric pressure. We report on evidence for a transition in Bi at about 740 °C, accompanied by a structural rearrangement. The evidence consists of a discontinuous change in the density at this temperature associated with an endothermal latent heat and a change in the structure factor over a relatively narrow temperature range.

Results and discussion. – We have measured at high temperature resolution and high accuracy, the temperature dependence of three physical properties of

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the liquid metal: density by means of gamma attenuation, heat capacity by means of differential thermal analysis (DTA) and static structure factor, $S(q)$, by neutron diffraction. The measurements were carried out on high-purity (5N) bismuth in an atmosphere of an ultrahigh-purity inert shielding gas (Ar, He).

The density was obtained by the γ-ray attenuation method, using a ^{137}Cs high-energy (662 keV) γ-ray source [1]. In order to avoid gas/air bubbles confined in the sample, prior to the measurement, the bismuth sample was cast into a cylindrical quartz tube under vacuum. The sample was then mounted inside a heated quartz crucible with a rectangular (7×7 mm) cross-section. The density, ρ, at each point was calculated from the attenuation of the γ-ray intensity, I, in which $\rho = \frac{1}{\mu d} \ln \frac{I_0}{I}$, where μ is the linear absorption coefficient per unit mass and d is the sample's thickness. I_0 was measured separately using the same experimental setup, in the absence of the sample. The accuracy of this approximation can be tested at the melting point where we obtained a density of $10.00 \pm 0.01\,\mathrm{g/cm^3}$, in agreement with the accepted value of $10.05 \pm 0.05\,\mathrm{g/cm^3}$ [29]. The density of liquid bismuth was measured from the melting point to 1000 °C in discrete steps of 5 °C. In order to avoid thermal fluctuations of the sample, at each point and before starting data acquisition, the sample was allowed to reach thermal stabilization. The same procedure was implemented while measuring I_0.

DTA is a technique which measures the relative specific heat of the sample *vs.* a reference sample [30]. Essentially, the measured value is the difference of the electromotive force generated by both thermocouples attached to the sample and reference. DTA measurements were performed using a TA Instruments - SDT 2960 apparatus. The measurements were carried out at different heating rates. Each measurement was performed using a fresh sample.

Bismuth is an ideal element for neutron scattering measurements due to its high coherent scattering cross-section (9.1477 barns), its negligible incoherent scattering cross-section (0.0084 barns), and a very small absorption cross-section (0.0338 barns at $\lambda = 1.8$ Å) [31]. Neutron diffraction measurements were conducted initially at Glass Liquid and Amorphous Diffractometer (GLAD) at the Intense Pulsed Neutron Source at the Argonne National Laboratory. Time-of-flight measurements were carried out at seven different temperatures upon heating. Additional independent measurements were carried out at the 7C2 diffractometer at Laboratoire Leon Brillouin at Saclay in order to confirm and extend the results that had been obtained. In this latter case, the diffraction of a monochromatic beam ($\lambda = 0.7$ Å) was recorded. Measurements at 14 different temperatures were performed upon heating. In both experiments, a bismuth cylinder, 8 mm in diameter and 30 mm high, was used. The cylinder was mounted in a sealed quartz capsule. The quartz capsule (8 mm inner diameter and 10 mm outer diameter), containing the sample, was evacuated and filled with high-purity He to approximately 300 mm Hg after which it was sealed. Empty quartz capsule diffraction patterns were also determined, at two different temperatures in GLAD and seven different temperatures in 7C2. As a part of the data analysis procedure, these diffraction patterns were corrected for background, cell and furnace contributions, for multiple scattering and for inelastic effects [32–35]. In both cases, in order to validate absolute $S(q)$ values, a diffraction pattern was separately determined for a vanadium cylinder. The temperature was measured by thermocouples attached to the outer bottom of the capsule.

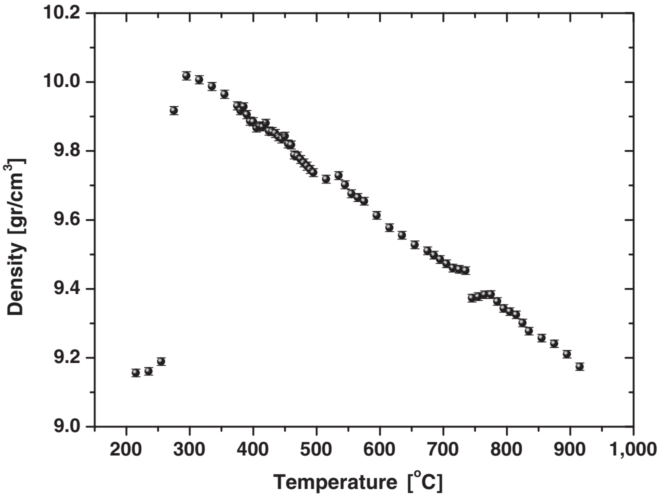

Fig. 1: Density of liquid bismuth as a function of temperature. At approximately 740 °C an irregularity of about 1% is observed (see text). The error of the measured points includes the systematic and statistical errors and does not exceed 0.1%. The upturn in density at about 275 °C corresponds to the melting of the measured sample.

The results of the density measurements are shown in fig. 1. The general tendency, as expected, is an expansion of the fluid with increasing temperature. The thermal expansion coefficient at the melting point, defined as $\frac{1}{\rho_m}\left(\frac{\partial \rho}{\partial T}\right)_P$, was $1.2 \times 10^{-4}\,\mathrm{K^{-1}}$, in good agreement with previous results [1]. However, at approximately 740 ± 5 °C an irregularity in the density appears. This feature might be interpreted as a discontinuous change in the density. This change in the density, of an order of approximately 1%, suggests the presence of a liquid-liquid structural transformation. This change is considerably larger than the experimental statistical error of approximately 0.1% observed in our measurements and was verified in several repetitions of the experiment using different samples. However, we note that it is considerably smaller than the density discontinuity measured in the LLPT in phosphorus [6] yet comparable to the density difference reported in yttria-alumina melts, $\sim 4\%$ [10].

To confirm the existence of such a transformation, we conducted a DTA measurement *vs.* a reference sample (Al_2O_3). In order to exclude the possibility of any chemical reaction having occurred between the sample and

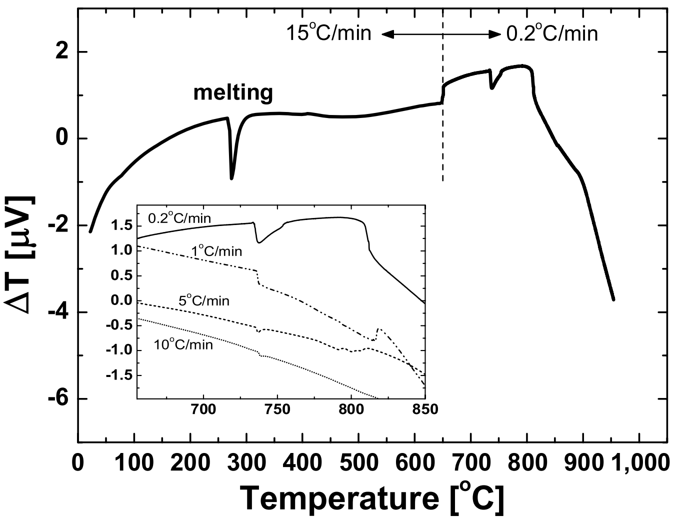

Fig. 2: Differential thermal analysis (DTA) of liquid bismuth showing the voltage difference between a reference and the sample expressed in microvolts (μV) a function of the sample's temperature. In addition to an endothermal peak associated with melting, an endothermal peak at 740 °C is observed. Possibly, an additional wide peak at about 810 °C is also observed. The inset shows the effect of the heating rate on the observed endothermal peak. The discontinuity at 650 °C is due to a change in the heating rate of the DTA apparatus.

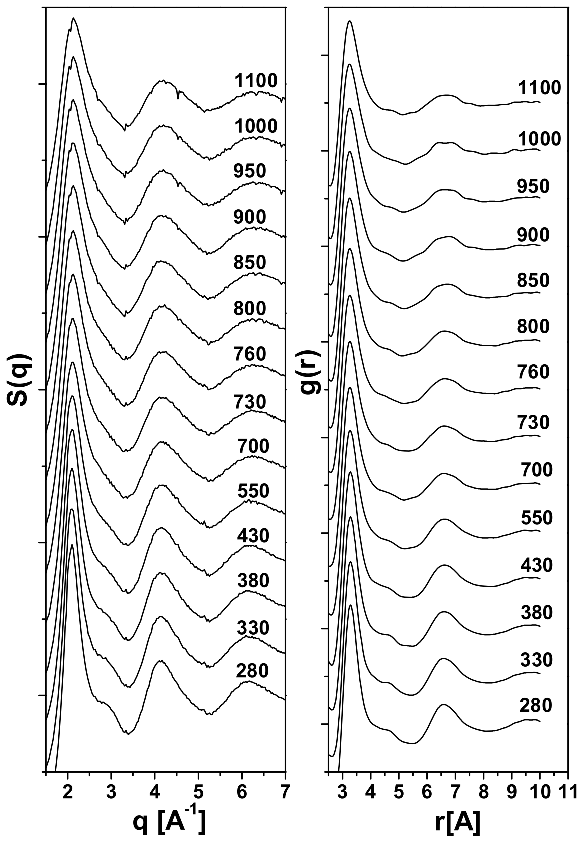

Fig. 3: Static structure factor $S(q)$ and pair distribution function $g(r)$ of liquid bismuth, measured on 7C2 diffractometer. Each curve is marked by the temperature in centigrade.

the crucible during the measurement, a meticulous visual inspection as well as a chemical characterization of the sample and the crucible were performed upon completion of the DTA measurement. The results of the DTA measurements are shown in fig. 2. In addition to the endothermal peak, associated with the melting of Bi, we observe an additional endothermal peak at 740 °C, the same temperature as that for the newly found density discontinuity. Such a peak implies the absorption of latent heat during the transformation. The existence of this peak is not sensitive to large variations in the heating rate, as seen in the inset of fig. 2. This transformation was also observed upon cooling as an exothermal peak. However, due to experimental constraints the cooling rate was relatively high and a hysteresis effect was observed. DTA is not a quantitative method for measuring latent heat, however, by comparing the area under the peak at 740 °C with that under the melting peak we can estimate a value of 0.02–0.1 kJ/mol for the latent heat of the proposed transformation. We note that this value is of an order of magnitude lower than that observed in typical solid-solid phase transitions, consistent with the general weakness of the present transformation. In passing, we observe an additional feature in the measurement that appears at approximately 810–820 °C. Recently, the temperature dependence of the electrical resistivity of liquid Bi was reported to exhibit an irreversible abnormal phenomenon beginning at 766 °C. That might be related to the present transition [28]. The authors [28] could not have seen the thermal feature at 740 °C because of the high scanning rate in their experiment.

An additional feature of this transition was determined by measuring the temperature dependence of the structure factor of molten bismuth —$S(q)$. We present the structure factor of liquid bismuth at several temperatures as measured by the 7C2 diffractometer in fig. 3 (left panel). Within the limit of experimental systematic errors [36,37], both the GLAD and 7C2 absolute $S(q)$ data are in reasonable agreement over the whole temperature range. Moreover, both our measurements near to the melting temperature (280 °C) are in good quantitative agreement with previous publications [24,25,36–39]. Pair distribution function curves ($g(r)$) were calculated for each $S(q)$ measurement. These curves are presented in fig. 3 (right panel). For clarity, $S(q)$ as well as $g(r)$ measured at GLAD diffractometer are only presented in fig. 5(C). At and above melting, both $S(q)$ and $g(r)$ curves are characterized by a shoulder located on the high q and r side of the first peak, respectively. This shoulder is common among the group-V elements, *i.e.*, As, Sb, and Bi. It has been suggested that the origin of this anomalous behavior results from a Peierls distorted A7 solid phase structure [40]. By observing fig. 3 (right panel) one can clearly observe the hard-sphere (HS) peak which consists

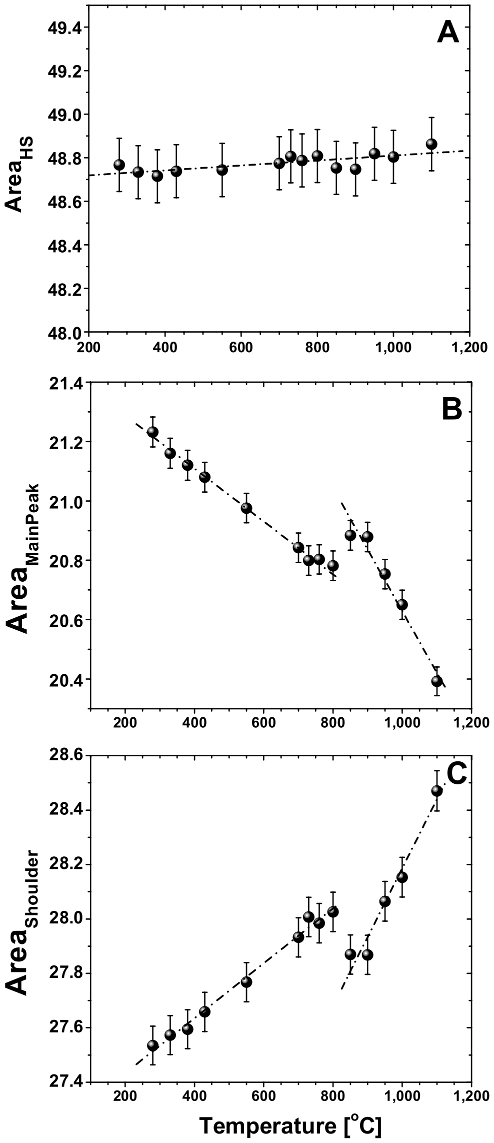

Fig. 4: Temperature dependence of the areas, defined by $\int_{r_1}^{r_2} r^2 g(r)\mathrm{d}r$, as calculated for molten bismuth at various temperatures (see text). Panel A: the area under hard-sphere peak, $\mathrm{Area}_{HS}(T)$; panel B: area under main peak, $\mathrm{Area}_{MainPeak}(T)$; panel C: area under the shoulder, $\mathrm{Area}_{Shoulder}(T)$. The lines shown in all panels are linear fit as a guide line.

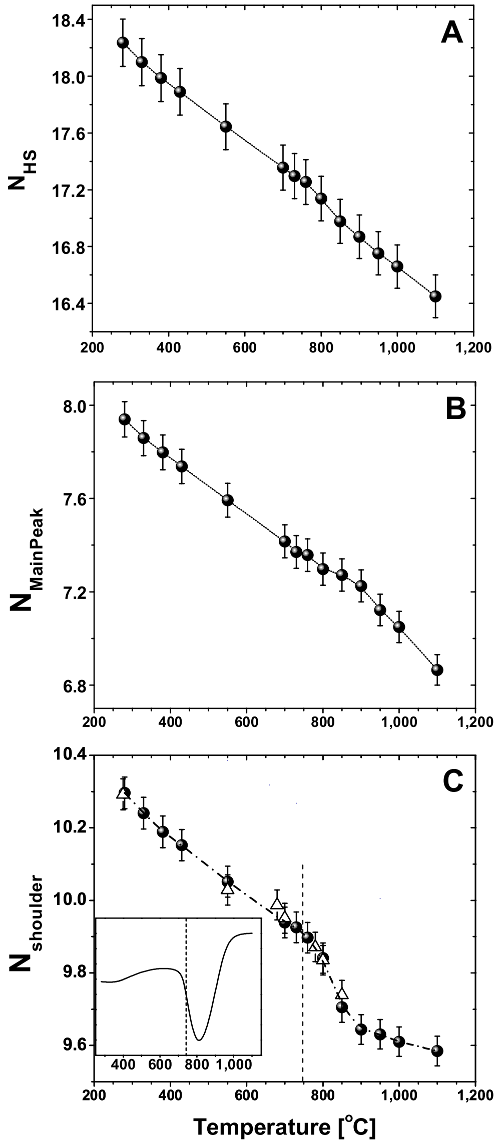

Fig. 5: Temperature dependence of the coordination numbers as calculated for molten bismuth at various temperatures. Panel A: the total number of atoms in hard-sphere peak, $N_{HS}(T)$; panel B: number of atoms in main peak, $N_{MainPeak}(T)$; panel C: number of atoms contributed by the shoulder, $N_{Shoulder}(T)$. The triangles show the data obtained from GLAD diffractometer. The inset of panel C shows the derivative of $N_{Shoulder}$ with respect to temperature. It should be pointed out that the density values used to calculate the last two points in this figure were linearly extrapolated from our measured density data.

of a main peak located at 3.28 Å and a shoulder at approximately 4.65 Å. The ratio of the positions of the peaks is approximately the square root of 2 which coincides with a simple cubic local order as has been previously observed [18]. The area under the peaks, defined by $\int_{r_1}^{r_2} r^2 g(r)\mathrm{d}r$, was calculated for the main peak ranging from 2.64 Å to 4.02 Å and the shoulder ranging from 4.02 Å to 5.40 Å. The temperature dependence of the area is shown in fig. 4. We observe that the temperature dependence of the total area (2.64 Å to 5.40 Å) is constant within the experimental error. However, the relative weight of the main peak and the shoulder are weakly temperature dependent. On this trend, we observe a discontinuity in the relative weight of the main peak between temperatures 750 °C and 800 °C.

By multiplying the area, presented in fig. 4, by the measured values of the density, we obtain the coordination number of atoms. The results are presented in fig. 5. Albeit, in doing this we risk smearing out the transition due to a possible mismatch between the two temperature measurements in the density and neutron scattering experiments. Indeed, the transition range broadens somewhat to about 100 °C. At the melting point N_{HS} is found to be about 18.25 atoms which is in good agreement with previous results [21]. The general tendency of N_{HS} is to monotonically decrease from 18.25 ± 0.15 at 276 °C to 16.45 ± 0.15 at 1100 °C. At the melting point the inner, main peak represents 8 atoms and the shoulder represents the remaining 10 atoms. As the temperature is increased the occupation of the main peak decreases to approximately 7.3 atoms at which point the transition occurs. Within the experimental error, both GLAD and 7C2 diffractometers data yield the same results. This is illustrated in fig. 5(C). From our neutron diffraction analysis we therefore associate this temperature-driven transformation with a structural change. We note in passing that, unusually for liquid metals [41], the positions of the first and the second peaks in the structure factor curves are independent of the temperature over the entire measured temperature range.

One possible explanation for our observations comes from a tight-binding simulation on liquid group-V elements [42]. The authors have shown that the low coordination number in liquid As is associated with a quantum-mechanical Peierls distortion of the local structure, yet in heavier elements with higher coordination numbers, such as liquid Sb and probably Bi, this effect is much weaker. As the density of liquid Bi decreases with temperature, the number of nearest neighbors is also observed to decrease, which could lead to a small but abrupt change in the strength of the Peierls distortion in the liquid. However, temperature-dependent quantum-mechanical simulations on liquid Bi are needed to ascertain the magnitude of this effect on the structural and thermodynamic properties.

Our results are in agreement with previous, lower resolution, studies of the temperature dependence of the structure factor of liquid bismuth obtained by neutron diffraction [22]. From changes in the shape of the intensity curve and in particular the disappearance of the $S(q)$ first-peak shoulder, the authors [22] concluded that a rearrangement in the short-range order occurs in the liquid between 550 °C and 830 °C, in reasonable agreement with our findings. Later studies [24,25] were not analyzed in the context of a possible transition, but are in very good agreement with the previous [22] and present measurements.

As shown in figs. 1 and 2, the structural transformation we observe has a positive specific volume discontinuity, $\Delta V > 0$, and a positive latent heat, which implies a positive entropy jump, $\Delta S > 0$. The Clausius-Clapeyron equation relates the slope of a phase transition line in the P-T diagram to these thermodynamic quantities, $\frac{\mathrm{d}T}{\mathrm{d}P} = \frac{\Delta V}{\Delta S}$, implying that the slope of this liquid-liquid transformation line is positive and very large, approximately 2×10^{-6}–$10^{-5}\,\mathrm{K \cdot Pa^{-1}}$, because of the low value we find for the latent heat of this transition. Based on volumetric measurements, a phase diagram of liquid bismuth at pressures of 1–10 GPa was proposed in [2]. The measured (L')-(L'') coexistence phase line terminates in at about 760 °C and 1.5 GPa with a negative slope. It is not clear whether this phenomenon is consistent with the present observation or other effects might be found at lower pressures and higher temperatures. Additional work under pressure, which is beyond the scope of the present study, will be required to resolve this issue.

Conclusions. – In conclusion, we have directly observed evidence for a temperature-driven liquid-liquid structural transformation at atmospheric pressure in molten bismuth at a temperature well above the liquidus. The existence of this transformation is supported by density and thermal measurements and by a change in the temperature dependence of coordination number obtained from neutron diffraction data. The magnitude of the change in the physical quantities across this transition is very small. Such a transition, at ambient pressure, challenges our fundamental understanding of liquid metals at elevated temperatures as simple fluids having properties that vary continuously with temperature. Additional studies are required in order to determine the exact nature of this newly found structural transformation, in particular to determine if it is a phase transition and its pressure dependence in the P-T phase diagram.

* * *

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